2

Concrete properties

2.1 Introduction

The art of manufacturing concrete -called Opus Caementitium- was first mastered by the Romans and the concrete technology was at its first flourishing time during the Roman Empire. Many constructions built at that time -aqueducts, amphitheater, bridges, temples (one of the most impressive is the Pantheon in Rome) - represent in our days a proof of durability. Yet, the use of cementing materials was known earlier, by the ancient Egyptians (calcined impure gypsum was a good bound) but the technology was not as advanced. The first 'concrete' in history consisted of calcined limestone mixed with lime and water, sand and crushed stone or brick and broken tiles. For constructions underwater, Romans ground to the lime, a volcanic ash that helped its hardening. With the decline of the Roman Empire in the fifth century, their art of manufacturing concrete was lost. A similar technique was reborn in the middle of the 19^{th} century when Portland cement was discovered in England. A burst of concrete technology

followed a short time after, with the manufacture of the reinforced concrete in France. A new age of concrete-based constructions opened, serving as a powerful tool for the Industrialisation of entire Europe. Originally concrete was produced by combining only three materials: cement (usually Portland cement), aggregate (sand and gravel) and water. In time concrete technology developed by improving the strength and durability of the final product. One of these techniques was adding into the mix very small quantities of chemical products or introducing, as an economic filler (cheaper than cement powder) and various inorganic materials. Ecological concerns encouraged this technique further, by using as a filler industrial rest products: blastfurnace slag, fly ash or silica fume.

One side effect of such 'ecological concrete' is related to its radiological aspects. Some of these fillers are, due to the extraction of the principal material, enhanced in concentrations of radionuclides of which ^{238}U potentially leads to an increased radon release. To investigate the mechanism of radon generation, transport and release in concrete, one necessarily needs to understand how concrete microstructure forms and develops. Moreover, one has to understand how this microstructure relates to the observed macroscopic properties of concrete.

This chapter presents a selection of information taken from a large amount of literature on various aspects of concrete and serves as a basis of knowledge for the general aim of this thesis. As cement is the bonding agent between the other components that form concrete, its manufacture, composition and hydration will be reviewed (section 2.2). As the samples studied in this thesis contain *ground granulated blastfurnace slag* (*ggbs*), the peculiarities of this type of cement will be surveyed. Secondly, a summary of the properties of the aggregate particles and some of the requirements imposed on them when enclosed in the mixture will be given (section 2.3). The microstructure of concrete and its dynamical character due to the ongoing process of hydration constitute another issue discussed in section 2.5 and section 2.4 of this chapter. The amount of water in concrete is a decisive parameter for the different types of porosities that are formed, their space distribution and connectivity thereby influencing the transport properties of concrete. The different forms in which water is present in concrete and conditions for its ingression are described in section 2.6. When cement and aggregates are mixed to form concrete, a very heterogeneous, multi-phase material is obtained. Although both the cement-paste matrix and the interface zone between cement paste and aggregate particles are important for the transport properties of concrete, under some conditions, it is a good approximation to consider only the cement paste as being representative. An example of the distribution of rel-

ative volumes of different phases in cement paste is given in section 2.7 together with some basic equations. The variables influencing the transport properties of concrete together with some values for the effective diffusion coefficients are briefly summarised in section 2.8.

2.2 Cement: manufacture and composition

The cements of interest in the making of concrete are called hydraulic cements because they have the property of setting and hardening underwater by virtue of a chemical reaction with water. Hydraulic cements (classified as: natural cements, Portland cements and high-alumina cements) consist mainly of silicates and aluminates of lime. Calcareous material and silica-, alumina-, and iron oxide-bearing materials (clay or shale) are the raw materials from which cement is obtained. The primary materials are first ground and thereafter burned at a clinkering temperature (of up to about 1450 °C) in a large rotary kiln where they sinter to form a series of more complex minerals. The resulting mixture, called *clinker*, after cooling is interground with gypsum to prevent the violent reaction of the tri-calcium-aluminate with water during hydration. After satisfactorily grinding the size of the cement particles becomes about 70 μm; conform to American standards [89], the optimal size of the cement particles should be about 45 μm. An indication of the degree of fineness of cement and powder materials, is given by the amount of *surface area* per unit mass ($m^2\,kg^{-1}$), usually expressed as Blaine value. This physical unit, characteristic for a certain type of cement, will actually be used throughout this thesis. The degree of crystallisation and the amount of amorphous material present in the cooled clinker depends on the rate of cooling. Assuming that cement is in frozen equilibrium, i.e. the cooled products reproduce the equilibrium existing at clinkering temperature, the same oxide composition is expected also for the cement powder. The oxide content is usually measured at clinkering temperature.

Table 2.1 presents the major mineral constituents of cement together with their usual abbreviations in the standard concrete terminology[1].

The mixing and grinding of the raw materials occurs either in water (wet process) or dry (dry process). The choice of process used in cement manufacture depends on the hardness of used raw materials and on their moisture content (for the dry process, the raw meal has to have a moisture content of about

[1]The standard notation in concrete technology associates the following symbols to the following oxides: C≡CaO, S≡SiO_2, A≡Al_2O_3, F≡Fe_2O_3.

Table 2.1: Main compounds of cement, their chemical form and the usual abbreviations.

Compound	Oxide composition	Abbreviation
tricalcium silicate	$3CaO \cdot SiO_2$	C_3S
dicalcium silicate	$2CaO \cdot SiO_2$	C_2S
tricalcium aluminate	$3CaO \cdot Al_2O_3$	C_3A
tetracalcium aluminoferite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF

0.2%). Nowadays the dry process is predominantly applied to minimise the energy consumption. No matter what process is used, an intimate mixture of the raw materials is required because part of the reactions that take place occur by diffusion in solid materials, and a uniform distribution of materials is essential to ensure a uniform product.

Often cement is considered to be formed mainly of C_3S (50-60%) ([78], [135]), a compound identified by its small, equidimensional colourless grains and known to have a high reactivity with water. The second compound, C_2S occurs in the cooled clinker preserved in its β-labeled form (the α-C_2S exists at high temperature; with temperature decrease it converts successively to β, γ and δ forms), recognised by its rounded grains, usually showing twinning. The other two compounds, C_3A and C_4AF, containing alumina and iron, form rectangular crystals and a solid solution, respectively. A few mass percentages of cement is held by the minor compounds (Na_2O, K_2O, MgO, TiO_2, Mn_2O_3). Their reaction with some aggregates constitutes a mechanism that contributes to the deterioration of concrete [78]. The observed reactions of the oxides of sodium and potassium (also called the alkalis) with the existent silicas in concrete lead to the occurrence of cracks thus, to a reduction in concrete durability.

Besides the Ordinary Portland Cement (abbreviated as OPC and classified as type I cement), there are many cement types being produced, i.e. Composite (pozzolana, fly ash, silica fume) Portland Cements (type II), Blastfurnace Portland Cement (type III), Pozzolanic Portland Cements (type IV) etc.

2.2.1 Blastfurnace Portland Cements

In this thesis Blastfurnace Portland Cement will be investigated and hence some of its properties will be briefly reviewed. *Blastfurnace Portland Cement* is a combination of Portland cement clinker and ground granulated blastfurnace slag, *ggbs*, a rest product of both iron and steel industries. It is obtained by a quick cooling of the slag followed by grinding. Its chemical composition (in oxides) is

similar to that of Ordinary Portland Cement (lime, silica, alumina) only they occur in different proportions (Table 2.2).

The European Standard *ENV 197-1:1992* recognises three classes of Portland blastfurnace cement: III/A, III/B and III/C based on a different ratio between the Portland cement clinker and the ggbs. The slag percentage for each of the classes is 36-65%; 66-80% and 81-95%, respectively. The Blastfurnace cement produced by the Dutch company ENCI at the IJmuiden plant is of **CEM III/B 42,5 LH HS** type and consists 25% of Portland cement clinker, 75% of blastfurnace slag and for a small amount of calcium sulfate ($CaSO_4$) that acts as a reaction regulator. Calcium sulfate is present as gypsum, anhydrite or a mixture of the two, in mineral or by-product form, and allows for a later control of the hardening process of the cement after combination with water. Based on its properties (summarised in Table 2.2), the Blastfurnace Portland Cement belongs to the category 'cement with **L**ow **H**eat of hydration'. Because the slag content of the Blastfurnace cement CEM III/B is higher than 65%, it satisfies the requirements for cement with **H**igh resistance against **S**ulfate attack (**HS**). A secondary effect due to the presence of the blastfurnace slag in the cement powder is the prevention of damage due to alkali-silica reaction and intrusion of chlorides. According to the normatives, the compressive strength of the concrete manufactured from this type of cement has to be in the range **42,5** to $62.5\,\mathrm{N\,mm^{-2}}$ after 28 d.

Table 2.2: Chemical composition (in oxides) of Portland Cement and blastfurnace slag cements [9].

Compound	Portland	Blastfurnace
	%	%
CaO	60-67	40-50
SiO_2	17-25	30-40
Al_2O_3	3-8	8-18
Fe_2O_3	0.5-0.6	ca.1
MgO	0.5-4	0-8
SO_3	2-3.5	ca.3
alkalis	0.3-1.2	ca.0.6
slag content	-	ca.76
heat of hydration $\mathrm{kJ\,kg^{-1}}$	400-500 [89]	250-400
specific gravity $\mathrm{kg\,m^{-3}}$	3150	2950
specific surface area $\mathrm{m^2\,kg^{-1}}$	-	390 ([9], [89])

Peculiar for ggbs is its glass structure (responsible for its reactivity), only a few percent consisting of crystalline matter and other minor constituents. Primary crystallisation products that occur when glass is formed are melilite (mixture of $2CaO{\cdot}MgO{\cdot}2SiO_2$ and $3CaO{\cdot}Al_2O_3{\cdot}SiO_2$) and merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$), the latter greatly influences the reactivity of the slag. The individual chemical units in the glassy structure of ggbs are unsystematic and irregularly arranged.

2.3 Aggregate properties

Since cement is the most expensive component of concrete, it is desirable to minimise the cost of concrete by using the smallest amount of paste and still achieve the desired strength and durability. Aggregates are mainly used as filler but they also provide concrete with better stability and resistance to deterioration. The amount of paste depends on the void space that must be filled and the total surface area of the aggregate that must be coated such that, during mixing, a good lubrication between aggregate particles is realised. The porosity of a mix of approximately spherical aggregate particles is smaller for a wide size distribution. This is the reason why a range of sizes is used in industry, the smaller particles can pack between the larger thereby decreasing the void space and lowering the paste requirements ([78], [89], [135]). To be able to select the optimal proportion of granular materials, certain additional properties of the aggregate must be known.

Granular aggregates, derived from natural rock, crushed stone, natural gravel and sands or lately also manufactured from industrial rest-products, occupy about 70 to 80% of the volume of concrete. The size of aggregates used in concrete ranges from particles with diameters in the range from 0.05 to 50 mm. A main division of aggregates is between *fine aggregate* (sand and fine pebbles), with sizes ranging from 63 μm to 4 mm, and *coarse aggregate* comprising material at least 5 mm in size. However, the usual classification in the technology of concrete is made on basis of specific gravity (the mass divided by the volume of the solid material excluding all pores) as heavyweight, normal-weight and lightweight [78]. The maximum aggregate size (usually around 25-40 mm) results from a compromise between the gain in strength due to reduced water requirements (the larger the size of the aggregate, the smaller the surface area to be wetted per unit mass) and the weaker bonds due to the discontinuities introduced in the mix ([78], [65]). As previously mentioned, the particle size distribution, or grading, is selected such as an optimal packing is achieved. An ideal aggregate

particle, that most natural sand and gravels come close to, is one that is close to spherical in shape (well rounded and compact) with a relatively smooth surface (this also results in the smallest surface-to-volume ratio). Crushed stones are much more angular (higher surface-to-volume ratio) and have a rougher surface texture. Thus, they reduce the movement of adjacent particles and require more paste for full coating ([78], [107], [89]).

Aggregate's chemical and mineralogical composition is another important factor to account for; the presence of any undesirable impurities (silt, clay, dirt or organic matter) modifies the properties of the aggregates and may interfere with the cement-aggregate bond and cement hydration. The bond with the aggregate is better if the latter has a rougher surface (due to mechanical interlocking); for softer, porous and mineralogically heterogeneous particles (limestone and siliceous aggregates), some chemical bonds may exist. In addition, porosity, permeability and absorption properties of the aggregate influence the bond with the hydrate paste, the water requirements of concrete and also its resistance and chemical stability.

2.4 Hydration of cement

One can regard concrete at different levels. In the simplest picture aggregate particles are distributed in a matrix formed by a cement paste. The cement paste is a combination of cement and water in a certain ratio (the *water-cement ratio*); its bonding properties are a result of its hydration. A schematic picture of the hydration of a single cement particle is presented in Fig. 2 (colour plate section). Initially, when water and cement are mixed, water will fill the empty spaces between the cement grains. After this initial contact, water will start hydrating the cement particles that will begin to dissolve/blend. The reaction products (very low soluble in water) precipitate as an outer layer. The inner products (*2* in Fig. 2 in the colour plate section), consisting of partly hydrated cement and forming a more consolidated layer, will first surround the unhydrated core (*1* in Fig. 2 in the colour plate section). Only fully hydrated products (*3* in Fig. 2 in the colour plate section) will be deposited in the water-filled space (*4* in Fig. 2 in the colour plate section) giving the impression of flocculation of the surface. The process of hydration can be regarded as the expansion[2] of the cement particles into the surrounding water filled space by way of their newly formed hydration

[2]The process of expansion of cement particles during hydration is referred to as growth in the concrete literature.

products. At any stage of hydration the cement paste contains unreacted powder particles, hydrates of various cement compounds (calcium silicate hydrates, calcium hydroxide crystals, traces of other mineral compounds) and large void spaces partially filled with water. Hydration products do not contain only solid hydrates but also the interstitial space between them: the newly generated pore space thus being a product of hydration.

The gradual reduction in size of the initial cement particle as result of hydration has been observed under a microscope. It was found that, in contact with water, the grains of cement were hydrated up to a depth of 4 μm after 28 days and to 8 μm after a year [52]. Calculations [100] show that, under continuous contact with water, only cement particles smaller than 50 μm will be fully hydrated. As the initial size of the cement particle decreases, the hydration rate decreases due to the reduction of the available amount of water. The space initially filled with water (the *capillary pore space*) is replaced by the uniformly growing hydrated grains of cement. Bonds with various degrees of strength are established in the cement paste leading to its consolidation.

In Fig. 2.1, the properties of the cement paste are schematically summarised. It starts from early beginning in the interaction of elements and oxides in an cement clinker to form the cement compounds and end by the formation of hydration products and capillary pores.

The chemical/stoichiometric reactions of cement components (see also Table 2.1) that mainly describe the process of hydration are:

$$2C_3S+6H \rightarrow CSH+3CH; \tag{2.1}$$

$$2C_2S+4H \rightarrow CSH+CH; \tag{2.2}$$

$$C_3A+6H \rightarrow C_3AH_6; \tag{2.3}$$

$$C_4AF+2CH+10H \rightarrow C_3AH_6+C_3FH_6, \tag{2.4}$$

where standard notations[3] from concrete technology are again used.

The main products in the cement paste are calcium silicate hydrates, *CSH*, and calcium hydroxide, *CH*, resulting from the reactions of C_3S and C_2S with water. *CSH* exist in a variety of forms (the dominant one is that of fibrous particles typically of 0.5 μm to 2 μm long and 0.2 μm across), their physical structure being very disordered. On the contrary, *CH* occurs in the form of thin hexagonal plates, up to tens of micrometers across, which at later stages of hydration grow into a massive deposit.

[3] $H \equiv H_2O$, $CH \equiv Ca(OH)_2$, $CSH = C_3S_2H_3 = 3CaO \cdot 2SiO_2 \cdot 3H_2O$.

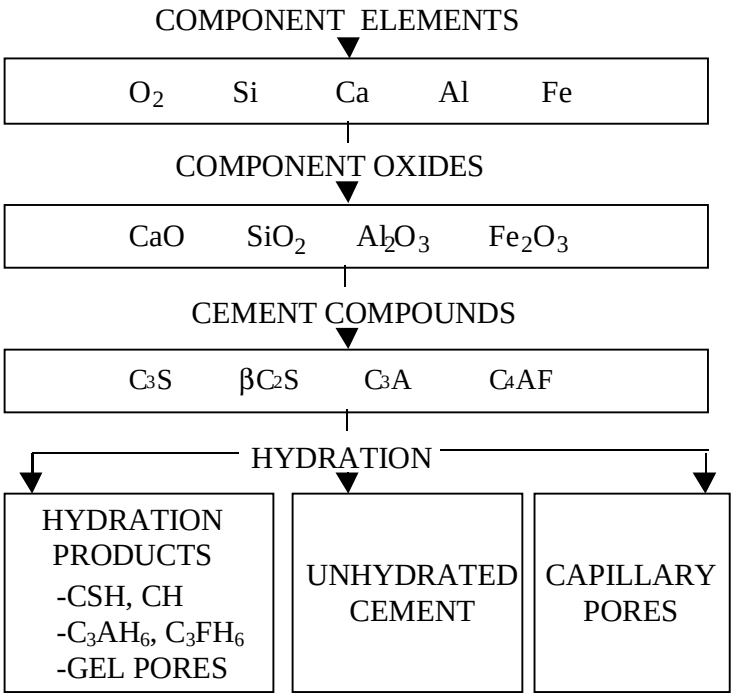

Figure 2.1: Schematic representation of the formation and hydration of Portland cement [89].

A small initial amount of gypsum ($CaSO_4 \cdot 2H_2O$) exists already in the cement, to prevent the violent reaction of C_3A with water (which otherwise would lead to immediate stiffening of the paste). The reaction products of C_3A with gypsum form a protective coating on the surface of the unhydrated C_3A particles, retarding its further reaction. The aluminate and ferrite phases produce in a first stage ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) and gypsum, the final products (having the stable form of cubic crystals) being the calcium aluminate and ferrite hydrates, C_3AH_6 and C_3FH_6, respectively. Although they are present only in small amounts, they have relevance because of their structural relationship with the other phases in cement.

Although not completely correct, the *CSH* phase is usually considered to form the cement *gel*. This gel may be considered as a product of hydration and stands for the cohesive mass of hydrated cement, including the gel pores. Gel pores are interconnected interstitial spaces between the gel particles, in form of

needles or foils. It is assumed that hydration products can not precipitate in pores having diameters smaller than about 2 nm [101], and this is consequently being considered as the diameter of a stable gel pore. Because the gel is porous it can hold large quantities of water.

The stoichiometric hydration reactions are exothermic. Thus, one of the methods used to determine the progress of hydration is by observing the evolution of the released heat. Initially, after a first contact with water, a rapid release of calcium hydroxide appears, leaving the unhydrated cement particles with an approximately 10 nm thick ([78], [89]) outer layer of *CSH*, that for a certain time period retards a further hydration. The process of heat release is also important for the properties of concrete. As in general concrete is known to have a low thermal conductivity, during hydration its internal temperature rises. Because the exterior of the concrete cools faster, a temperature gradient occurs that may cause cracking. The released heat of hydration causes loss of water thus being also responsible for the shrinkage of the cement paste and of concrete [135]. To prevent shrinkage and to achieve a good quality of the product, the appropriate mix has to be placed in a suitable environment during the early stages of hydration. The procedure used to promote the process of hydration of cement via control of temperature and moisture movement from and into the concrete is called *curing*. Ideally, concrete remains water-saturated to a large degree until the originally water-filled space in the fresh cement paste has been filled to the desired extent by the products of hydration. Hydration at a maximum rate can proceed only under conditions of water saturation and it is greatly reduced if the relative humidity in the capillary pores drops below 80%. The mostly used methods for curing of concrete are water curing (continuous contact with water of the concrete surface) and membrane curing (the surface of concrete is covered with polyethylene sheeting to prevent loss of water).

The rate of hydration and its heat release depend on the temperature at which hydration takes place, on the compound composition (type) of cement, on the quantity of cement in the mix and on the fineness and particle-size distribution of cement. It may at first seem best for cement to be as fine as possible, to have a high hydration rate. However, this would also imply a higher rate of early heat evolution and desiccation leading in time to a more rapid deterioration of concrete when exposed to ambient air.

When Blastfurnace Portland Cement is mixed with water, the Portland cement components begin to hydrate first and only a small amount of *ggbs* has an

immediate reaction, depending upon the breakdown of the glass[4] by the OH^- ions released during the hydration of Portland cement. *CSH* are formed as a result of the reaction of ggbs with the gypsum released by Portland cement. The progressive release of alkalis by the ggbs together with the formation of gypsum by Portland cement, results in a continuing reaction of *ggbs* over a long period. Hydration of ggbs produces more *CSH* and less lime than Portland cement alone as the blend has a higher content in silica and less lime than Portland cement alone. *CH* plays a very important role in the process of hydration of blended cements (mixture of Portland cement with blast furnace slag and/or fly ash). Both *ggbs* and fly ash are unable to continue their reactions without the *CH* produced during hydration of C_3S and C_2S.

2.5 Microstructure of concrete

The microstructure of concrete together with the chemical bonds influences most properties of concrete. It depends not only on the original packing of cement and aggregate particles, the water-to-solid ratio, the mineral admixtures but also on the ulterior conditions under which hydration proceeds (temperature, relative humidity, curing etc.). Available information of the solid phase is achieved from studies on the shape and size, bonding of the surfaces, surface area and even density while those on the non-solid phase address to porosity, pore shape and pore-size distribution. To add to the complexity, all these properties are interdependent. The morphology of the solid phase has been described in the previous section, this section will focus on the description of the void phase. In the most general way, the different types of pores present in concrete (gel pores, small and large capillary pores, closed pores, ink-bottle pores, porosity associated with paste-aggregate interfacial zones, microcracks, porosity in aggregate, voids and entrapped air) and the way they are distributed, define the microstructure of concrete [96]. For practical reasons concrete porosity is divided into two classes [24]:

· the porosity in the paste matrix, estimated from investigations on the cement paste.

· the porosity associated with the aggregate and paste interface, that contains also microcracks, determined directly on aggregate-containing materials.

[4]During the formation of cement clinker in the kiln about 30% of the material becomes liquid that by subsequent cooling crystallises. However, a certain fraction will undercool to glass.

Immediately after the mixing of cement paste[5], water surrounding the dry cement grains is considered to fill and actually form the whole network of *capillary porosity* (small and large pores with diameters of the order of μm). The capillary porosity depends on the water-cement ratio and on the degree of hydration, at any stage the capillary pores represent that part of the volume that has not yet been filled by the products of hydration. In well-hydrated, low water-cement ratio pastes, the capillary pores range in sizes between 10 to 50 nm while at high water-cement ratios, at early stages of hydration the capillary pores can be as large as 3 to 5 μm [78]. As hydration proceeds, the amount of hydration products increases and the gel pores will block at a certain time the capillaries, introducing discontinuities in the network of capillary pores so that they turn into pores interconnected only by gel pores. The lower the water-cement ratio, the earlier this segmentation occurs ([47], [89], [107]). For a water cement ratio of 0.48 the approximate time-scale at which capillaries become segmented is between 7 and 14 days. For each type of cement, for a certain value of the water-cement ratio (lower than 0.5) all cement is hydrated and all capillary pores removed. These mixtures are thus, very compact. However, if one increases the water-cement ratio, all the cement can hydrate with the compromise that also capillary pores will start being present.

It was mentioned before that a nominal diameter of the *gel pores* is around 2-3 nm (one order of magnitude greater than the size of water molecules) and it is also a well-known fact that gel pores occupy about 28% of the total volume of the gel meaning that gel of similar properties is formed at all stages [99], i.e. particles of the same size are constantly produced and the already existing gel particles do not grow in size. Two types of bonds are assumed to be responsible for the cohesion of the gel: one is due to the physical attraction -Van der Waals forces- between solid surfaces separated only by the gel pores; the other is related to the chemical bonds linking the gel particles and known to be much stronger than Van der Waals forces [135]. Gel pores are known to be important for the hygroscopic properties of a porous material (water-vapour sorption characteristics). They seem to concentrate at some sites in the hardened paste forming isolated clusters of connected gel pores surrounded by larger capillary pores [96].

Between gel and capillary pores (i.e., between 2 nm and 50 nm) a *transition domain* is situated where electrostatic interactions between the pore walls and the liquid extend over a significant fraction of the cross-sectional area.

[5]Usually cement paste in concrete occupies from 23% to 36% of the total volume, fine aggregate between 25-30% and coarse aggregate fills the remaining volume [90].

Most investigations on cement paste show a broad pore-size distribution [96]. The pores vary in shape but they form an interconnected system randomly distributed through the cement paste. A study on the cement paste [166] using mercury intrusion showed a threshold diameter that decreased with the amount of hydration. Some authors [161] consider 0.1 μm as the lower diameter limit of capillary porosity. Neville [89] considers that mature pastes contain few pores larger than 1 μm, most pores being smaller than 0.1 μm. The median size of capillary pores is 1.3 μm while gel pores are much smaller, having less than 2 or 3 nm in nominal diameter. Maekawa [71] uses the IUPAC classification with a radius of capillary pores ranging between 0.01 μm to almost 100 μm while the gel pores cover the 0.1 nm to 0.05 μm domain.

The fact that pore sizes are given as diameters is a convention; the pores are never only cylindrical or spherical in shape. The radius/diameter represents a sphere with the same ratio of volume to surface area. Only macropores (larger than 0.1 μm in diameter) come close to a spherical shape [78]. However, spherical pores may originate from residual air bubbles that may be entrapped or entrained during the mixing operation of concrete, or from imperfect cement particle packing. The size of the entrapped voids may be as high as 3 nm while that of the entrained bubbles ranges from 50 to 200 μm.

The second type of porosity in the classification above is related to the bond of an aggregate in the cement paste, also called the *aggregate-paste interfacial zone*. The interfacial zone is formed not only around a coarse aggregate particle but also around the fine ones. Some experimental investigations report that the thickness of the interfacial zone lies between 15 and 50 μm, the major differences from the structure of the bulk paste arising in the approximately first 15 to 20 μm from the physical interface ([80], [128], [71]). However, a constant thickness of the interface may be assumed for the case the aggregate particle size is very large compared to that of cement particles. In reality, the interface thickness depends on the aggregate particle size. For the same paste composition and at the same degree of hydration the presence of coarse aggregates results in an increased porosity; the presence of fine aggregates has a similar but smaller effect ([162], [71]). Experimental results sustained by computer simulations indicate that the porosity of the interfacial zone (especially near the aggregate surface) may be up to three times the porosity of the bulk cement paste ([144], [20]).

The presence of coarse aggregates associated with the shrinkage of the cement paste is considered of being the cause for the occurrence of *microcracks*. During drying, the cement paste splits away from the aggregate surface; the path of a

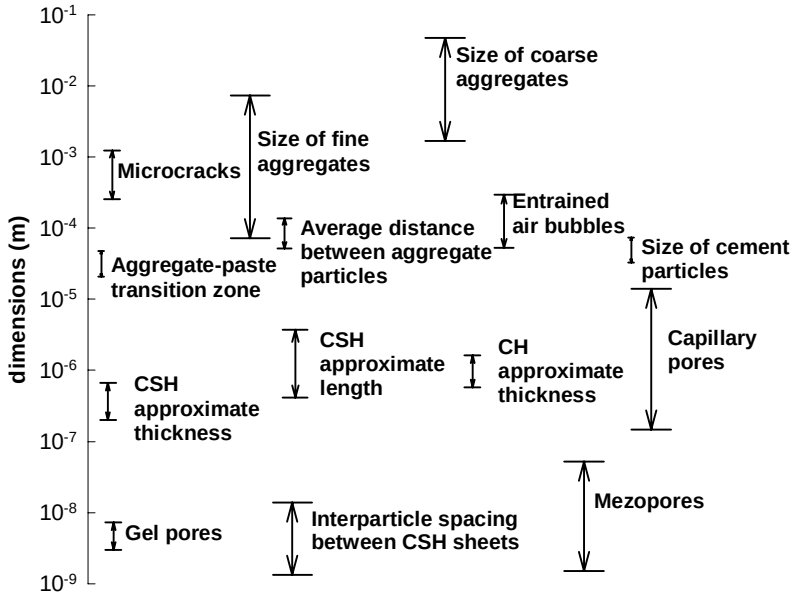

Figure 2.2: Dimensional range of solids and pores in the hydrated cement paste and concrete.

crack will tend to run along the weakest parts of the specimen and contribute to the bulk microstructure. Paradoxically, the coarse aggregates also act in preventing the opening of a single wide crack, heterogeneity of concrete being in a way beneficial. An upper limit of 0.1 mm has been suggested for these microcracks and as long as they are stable, they do not influence the concrete strength.

Consequently, in concrete, there are *discontinuities at any level*, however small. SEM investigations of Philippi *et al.* [96] on different mortars show that, with increasing magnification, one can scan through a broad range of sizes: from the grains of sand and air inclusions of the same mean width of 100-200 μm where the paste appears as an homogeneous material between the solid grains (magnification 25x); to an extended network of fissures (3 μm width) surrounding the grains and establishing bridges through the whole medium for fluid transport (magnification 200x) and finally to the products of hydration observed as porous islands, i.e. a network of gel and small capillary pores surrounded by larger capillary pores (magnifications above 3200x). Fig. 2.2 presents a summary of the

dimensions of different phases to be encountered in concrete.

For blastfurnace Portland cements, the paste microstructure was observed to become denser than that of ordinary Portland cement, its pore-size distribution being shifted to lower values (the median pore size is smaller). *Ggbs* has finer particles than Portland cement which improves the particle packing and ensures a better dispersion of the cementitious particles. Consequently, more of the pore space becomes filled with *CSH* [89] resulting in a higher amount of gel pores (lower amount of capillary pores [2]). An increase in the amount of ggbs is also generally known to reduce the water demand of the paste. However, for small water cement ratios the slag mortar displayed large pores and possible even microcracks in its structure. Microscopic investigations showed that concretes containing ggbs exhibit a more granulated structure than the typical homogeneous appearance of the paste in Portland cement concretes. This is likely due to a difference in the degree of reactivity of the component particles or the various manners of development. Prolonged moist curing of concrete containing ggbs is important because the initial low rate of hydration results in a system of capillary pores which allows the loss of water under drying conditions. If that happens, hydration will be terminated prematurely.

2.6 Water content of concrete

Water in concrete has a special role, it is present from the beginning and it is a necessary ingredient for the hydration of cement that will form the paste to hold the aggregates in the mixture together.

Generally, water in concrete consists of that added to the mix and that held by the aggregate at the time when it enters the mixer (the best choice for an equilibrium moisture state of aggregate in concrete is saturated surface dry, i.e. all pores filled with water but no film of water on the surface [81]). As the amount of water, filling the pores of the aggregate, interacts little with the paste it can be considered negligible. In the fresh paste, aggregates, cement and water are intermixed, the water forming a capillary system between the unhydrated cement particles. Enough water has to be present in the mix such that full hydration will be reached, i.e. for the filling of the gel pores being formed (*vapourisable water*) and for the chemical reactions with the silicates (*non-vapourisable water*)[6]. During hydration, the surface area of the solid phase increases and a large amount

[6]In concrete technology, vapourizable and non-vapourizable water are denoted by evapourable and non-evapourable, respectively.

of vapourisable water becomes adsorbed onto it. If during formation no water movement to and from the concrete is permitted, the gel is fully saturated with water. The gel water is strongly bound in the gel pores and cannot move in the capillaries to participate in the hydration of the still unhydrated cement. The amount of non-vapourisable water increases as hydration proceeds. In fully hydrated cement the proportion of non-vapourisable water is 23% by mass of the anhydrous material (dry cement) [69].

Although, as already mentioned above, one usually divides the water held in concrete between *vapourisable* and *non-vapourisable*, according to whether or not it can be removed, a more precise classification, indicating also the different degrees of firmness, is presented below ([89], [135]):

· *capillary water* contained in the capillaries with sizes greater than 0.05 μm; its removal does not cause any volume change in contrary with the water held by capillary tension in capillaries of size 2 to 50 nm (transition domain) which on removal may cause shrinkage of the system.

· *gel water* (Fig. 2 in the colour plate section)

  ○ *adsorbed water* molecules at the surface of the gel particles under the influence of attractive forces. It has been suggested that by hydrogen bonding up to six molecular layers of water can be held [78]. Its total removal causes shrinkage of the hydrated cement paste.

  ○ *interlayer* or *zeolitic water* situated between the surfaces of certain planes in a crystal (especially associated with the *CSH* phase) is usually a monomolecular layer held by hydrogen bonding and requires strong drying; this loss leads to a strong shrinkage of the *CSH* structure. It also does not move readily under the application of pore pressure gradients.

· *chemically combined (bound) water* with the silicates (part of the silicates solid structure).

Besides by the curing conditions, the history of concrete-water content is further influenced by the ambient humidity and temperature at which the concrete is stored. For example, if the relative humidity falls below 45%, the capillary pores dry out but the gel pores will still contain adsorbed water. Water ingression or removal at different structural levels depends on both relative humidity and temperature conditioning of concrete. Schneider [126] reports that when concrete is heated to 100°C, capillary water starts being lost. The amount of vapourisable/gel water is usually determined by the loss upon drying [107] at 105°C. At 180°C the adsorbed water is also removed. Dehydration of the *CH* begins at 500°C and finally, at even higher temperatures (around 700°C) the chemically

combined water in the *CSH* compounds is removed. In terms of relative humidity, it is experimentally known ([65], [71]) that even if concrete is exposed to the same conditions, its water content is different under drying and wetting. This hysteresis-type of behaviour is due to ink-bottle effects, differences in the energy of adsorption and desorption of water molecules to the microporous surface, etc. Thus, in the range 30-10% RH gradual removal of interlayer water from the edges occurs while for 10-2% RH further removal is accompanied also by shrinkage of the specimen. However, a significant amount of interlayer water resides in the *CSH* structure even at very low relative humidity, severe drying conditions being required to remove it [71]. Re-entry of water gradually occurs over the entire range of relative humidities.

2.7 Relative volumes

From the initial mix of cement and water, throughout the process of hydration, the distribution of the volumes of the products in the cement paste changes continuously. This distribution changes again when one adds the aggregates to the mix. It is thus worthwhile to try to relate the amount of the relative volumes to some preparation parameters (i.e. water-cement ratio, initial volume of cement/powder). To illustrate the evolution of the relative volumes in the hydrated cement paste, we will first define some of the employed terminology.

At any stage of hydration the *cement paste* consists of *unhydrated cement*, *hydration products* and *residual capillary space*.

1. The *unhydrated cement* consists of unreacted cement powder particles.

2. The *hydration products* (also called hydrated cement, gel product, gel paste or simply gel) are composed of:

· the *solid products of hydration* (gel solids), including *the solid products* and *the chemically combined water* (non-removable water). The fraction of non-vapourisable water[7], φ, expressed per unit mass of hydrated cement is usually determined from the stoichiometric reactions of hydration (section 2.4).

· the *gel pores*. At any stage of hydration the gel pores are considered water filled [89].

[7]In concrete terminology, the amount of chemically combined water is denoted by β. The same symbol in radon research denotes the partition corrected porosity that will be defined in chapter 4 of this thesis. As the main subject one investigates is radon, the decision was made to keep the radon notations.

· the *interlayer pores.* These pores comprise the volume of water residing between the layer structures of *CSH.*

Gel water includes besides the adsorbed water (present in the gel pores), the interlayer water (see also Fig. 2 in the colour plate section).

Independent on the degree of hydration of the powder, α, the characteristic gel porosity, ε_{ch} represents a fraction of 0.28 from the total volume of the gel (section 2.5).

3. The *residual capillary space* consists of water-filled and/or empty (air-filled) capillaries.

For a sealed specimen with no water movement to or from the system as well as for a specimen cured under water, at any stage of hydration α, the initial absolute volume of dry cement and water when initially mixed are equal to the volume of the cement paste, V_{paste} (m^3) consisting of unhydrated cement, hydration products and residual capillary space. As a general rule all volumes defined in what follows are expressed *per unit volume of the paste*:

V_p ($m^3\,m^{-3}$): initial relative volume of dry cement;
V_w ($m^3\,m^{-3}$): initial relative volume of water in the mix;
W_p ($kg\,m^{-3}$): initial relative mass of dry cement;
W_w ($kg\,m^{-3}$): initial relative mass of water;
V_{uc} ($m^3\,m^{-3}$): relative volume of unhydrated cement in the paste;
V_{gp} ($m^3\,m^{-3}$): relative volume of hydrated cement (gel products);
V_{gs} ($m^3\,m^{-3}$): relative volume of gel solids;
W_{gs} ($kg\,m^{-3}$): relative mass of gel solids;
V_{ccw} ($m^3\,m^{-3}$): relative volume of chemically combined water;
V_{gw} ($m^3\,m^{-3}$): relative volume of gel water;
V_{wc} ($m^3\,m^{-3}$): relative volume of residual capillary water;
V_{ec} ($m^3\,m^{-3}$): relative volume of residual capillary pores.

Using the notations above one finds:

$$V_p + V_w = V_{uc} + V_{gp} + V_{wc} + V_{ec} = 1. \tag{2.5}$$

The specific gravity of the products of hydration of cement is such that they occupy a larger volume compared to the absolute volume of unhydrated cement but smaller than the sum of volumes of the dry cement and the non-removable water because of the change in water density from liquid phase (ρ_w =997 $kg\,m^{-3}$ at 25°C and 1 atm) to that of chemically combined (ρ_{cw} =1250 $kg\,m^{-3}$) [89]. An average value of 2160 $kg\,m^{-3}$ for the specific density of the products of hydration is to be found in literature ([89], [78]). Powders consisting of pure Portland

cement have a specific density, ρ_c of 3150 kg m^{-3} while for blended cements an average specific density, ρ_p (kg m^{-3}) can be obtained as a weighted average:

$$\rho_p = \sum_i p_i \rho_i, \tag{2.6}$$

with p_i the proportion of the blend in the powder and ρ_i its specific density.

The preparation parameters to which one may relate the amount of relative volumes in the hydrated cement are the initial volume of dry cement, V_p (m^3 m^{-3}), and the water-cement ratio by volume, $\left(\frac{w}{c}\right)_V$. The initial volume of water in the mix can be thus calculated:

$$\left(\frac{w}{c}\right)_V = \frac{V_w}{V_p}. \tag{2.7}$$

Given the powder density, ρ_p, and the density of liquid water, ρ_w, the initial mass of powder per unit volume of the paste (W_p) can be determined from:

$$\left(\frac{w}{c}\right)_m = \frac{\rho_w V_w}{\rho_p V_p} = \frac{W_w}{W_p}, \tag{2.8}$$

where $\left(\frac{w}{c}\right)_m$ is the water-cement ratio by mass.

The volume of unhydrated cement/powder in the paste, V_{uc}, is simply:

$$V_{uc} = (1 - \alpha) V_p. \tag{2.9}$$

For a given water-cement ratio, the volume of chemically combined water, V_{ccw}, is

$$V_{ccw} = \varphi \frac{\alpha W_p}{\rho_{cw}}, \tag{2.10}$$

with φ the fraction of non-vapourisable water and ρ_{cw} (kg m^{-3}) the density of the chemically combined water. From the mass conservation between the gel solids, the hydrated powder and the chemically combined water we have that:

$$W_{gs} = \alpha W_p + \alpha \varphi W_p = \alpha (1 + \varphi) W_p; \tag{2.11}$$

$$V_{gs} = \alpha \frac{W_p}{\rho_p} + \varphi \frac{\alpha W_p}{\rho_{cw}} = \alpha W_p \left(\frac{1}{\rho_p} + \frac{\varphi}{\rho_{cw}}\right). \tag{2.12}$$

Because the paste has a characteristic porosity ε_{ch}=28%, and, by definition, it is the ratio of the total volume of pores in hydrated cement and the volume of hydrated cement:

$$\varepsilon_{ch} = \frac{V_{gp} - V_{gs}}{V_{gp}} = 1 - \frac{V_{gs}}{V_{gp}}. \tag{2.13}$$

Assuming that the gel pores are fully saturated, the volume of gel water, V_{gw}, can be determined as:

$$V_{gw} = \frac{\varepsilon_{ch} V_{gs}}{1-\varepsilon_{ch}} = \frac{\varepsilon_{ch} \alpha W_p}{1-\varepsilon_{ch}} (\frac{1}{\rho_p} + \frac{\varphi}{\rho_{cw}}). \tag{2.14}$$

Thus, by adding Eq. 2.12 and Eq. 2.14, the total volume of hydrated cement is:

$$V_{gp} = V_{gs} + V_{gw} = \frac{\alpha W_p}{1-\varepsilon_{ch}} (\frac{1}{\rho_p} + \frac{\varphi}{\rho_{cw}}). \tag{2.15}$$

Additionally, the dry density of gel products, ρ_g ($\mathrm{kg\,m^{-3}}$) can be obtained as the ratio of the mass of gel solids and the total volume of hydrated cement, V_{gp} ($\mathrm{m^3\,m^{-3}}$),

$$\rho_g = \frac{W_{gs}}{V_{gp}} = \frac{(1+\varphi)(1-\varepsilon_{ch})\rho_p \rho_{cw}}{\rho_{cw} + \varphi \rho_p}. \tag{2.16}$$

By knowing the volumes of non-vapourisable water (Eq. 2.10), that of gel water (Eq. 2.14) and the initial volume of the water in the mix, V_w ($\mathrm{m^3\,m^{-3}}$), the residual capillary water can be calculated from:

$$V_{wc} = V_w - V_{gw} - V_{ccw}. \tag{2.17}$$

Finally, the empty capillary space can be determined from Eq. 2.5 as:

$$V_{ec} = V_p + V_w - V_{uc} - V_{gp} - V_{wc}. \tag{2.18}$$

To exemplify the relations above, the hydration of a sealed paste (constant total volume) with a $\left(\frac{w}{c}\right)_m$ =0.48 and an initial amount of 126 g of pure cement (ρ_c =3150 $\mathrm{kg\,m^{-3}}$) is considered. From Eq. 2.8 and Eq. 2.7, this quantity corresponds to a volume of 40 ml of cement. From the same equations, the volume of water in the mix forming a capillary system between the unhydrated cement particles is 60 ml.

Let us first consider the situation when the cement has been fully hydrated ($\alpha = 1$), situation depicted in the right-hand side of the diagram in Fig. 2.3. At this stage, the volume of non-removable water is 0.23 of the mass of anhydrous cement (section 2.6). Consequently, the volume of the chemically combined water calculated from Eq. 2.10 is 29 ml. From Eq. 2.12 a volume 63.2 ml of gel solids is determined and, using this value in Eq. 2.13, the volume of gel water is 25.3 ml. Thus, the volume of hydrated cement is 88.5 ml and there are 5.7 ml of water left as capillary water in the paste (Eq. 2.17). In addition, empty capillaries

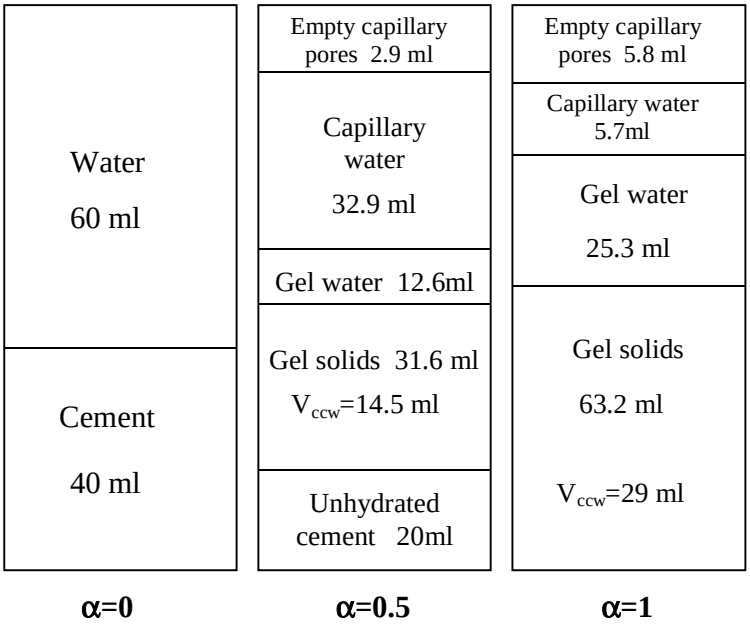

Figure 2.3: Volumetric proportions of cement paste composition at different degrees of hydration, α for an initial volumetric water-cement ratio of $\left(\frac{w}{c}\right)_V$ =1.5.

comprise 5.8 ml. From these values it can be calculated that, at 100% hydration, the gel/capillary space ratio is 0.89.

As a further illustration, the centre diagram shows the volumes of different components of the paste when only half the cement has hydrated ($\alpha = 0.5$). According to Eq. 2.9, half the cement powder (20 ml) will remain unhydrated and the non-removable water will be half the volume corresponding to full hydration. The other relative volumes are calculated in the same way as above. A total volume of 44.2 ml for the hydrated cement is calculated that corresponds to a gel/capillary ratio of 0.55.

The relative volumes of the products in the cement paste can be calculated for any other stage of hydration α using the procedure above.

In practice, the distribution of the volumes is once again changed when one adds the aggregates to the mix, for example the total void content consists besides capillary and gel pores also of an approximate amount of 1-3% of air entrapped in the mix. As also mentioned in Eq. 2.6, when an additional cementitious material

with a different specific gravity than that of Portland cement is present, density corrections have to be made. Theoretically, for any modification, i.e. the grading of the aggregates, their content of free moisture, corresponding corrections have to be introduced to fully describe the concrete. However, under some assumptions, the hydrated paste can be a very good approximation for concrete as a whole [71].

2.8 Transport properties of concrete

Transport properties of concrete are investigated mostly for reasons of durability. If the durability design is inadequate, deterioration of concrete occurs[8]. As transport of fluids in concrete depends essentially on the microstructure and on its penetrability and because of the highly heterogeneous and dynamic nature of this structure, it seems a difficult task to describe a certain transport parameter precisely [46]. Moreover, a broad knowledge of the important features of the structure of individual components of concrete is essential for understanding and controlling its properties. The two components of the structure essentially related to the transport phenomena are the hydrated cement paste and the transition zone. From the pores of the cement paste, the capillary pores, which form a continuous network are relevant for transport. Gel porosity plays only a major role during the process of hydration, but has a reduced contribution in transport processes of liquids or vapours. In the transition domain, transport processes are hindered because of the additional electrostatic interactions [77]. Air bubbles do not significantly affect the transport processes unless they are in some way connected to the 'open' network [2]. The same holds for the ink-bottle pores that are responsible for entrapping water and thereby for the observed hysteresis behaviour during drying and wetting. The impact of interfacial zones on transport properties is also primarily related to their chance of forming a continuous path throughout the concrete. Their influence is related to their large size and not so much to their total volume fraction. High water-cement ratio mortar mixes containing more than 45% by volume of aggregate may give rise to the interfacial zones that allow percolation of water. This situation contrasts with self-compacting high-performance concrete aggregates, which are fully enveloped by the cement paste. Their interfacial zones created at their surfaces are hardly con-

[8] In time, concrete is subject not only to aging and to environmental humidity and temperature changes but also has to withstand the action of aggressive ions, carbon dioxide, alkali reactions that will alter its pore structure, lead to the formation of microcracks, decrease its surface area, etc.

nected. With the present knowledge and the existent manufacturing techniques one can set the parameters characterising the admixtures such that concretes can be regarded uniform from the point of view of transport. Maekawa [71] concludes that -with a few exceptions- for most concretes encountered in practice, their transport properties are dictated by the transport properties of the cement paste matrix. For example, essentially the same values [92] are obtained for effective CO_2 diffusivities for concrete and for the corresponding cement paste, as function of relative humidity and concrete composition parameters.

Liquid water, water vapour and other gases (oxygen, carbon dioxide, etc.) are of interest for transport through concrete. In addition to water chemically fixed during the early stage of hydration, progressively most of the vapourisable water will be removed. Consequently, the pores will be left either empty or unsaturated. Bulk movement of liquid water occurs mostly through saturated capillaries by pore water pressures. Transport of vapours and other gases is dominant at low relative humidities and takes predominantly place via diffusion in the unsaturated gel pores. Ingress of moisture into the pores of concrete is driven by the external pressure and temperature gradients.

Different values of transport parameters in concrete have to be carefully compared and one has to correctly account for the differences in the mix parameters, curing and environmental conditions that may occur.